A FEASIBILITY STUDY OF THE IDENTIFICATION OF FUEL-CLADDING FAILURES USING SODIUM-SOLUBLE ISOTOPIC TAGS

R. J. Meyer, C. E. Johnson, and L. E. Ross

U of C-AUA-USAEC

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Chemical Engineering Division

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ABSTRACT

Two isotopic tagging methods for locating cladding defects in sodium-bonded fuels are discussed. Both methods rely on reactor activation of the tag while it is confined inside the fuel pin. One method uses ^{121}Sb and ^{197}Au, whose activation products are ^{122}Sb and ^{198}Au. The other uses ^{198}Pt and ^{197}Au, whose activation products are ^{198}Au and ^{199}Au. Varying the weight ratios of the stable isotopes produces distinctive disintegration ratios of the activation products. Each fuel element in a particular subassembly is tagged with the same distinctive isotopic mixture. Should a cladding of a fuel element fail, the tag is released into the primary sodium coolant. Identification of a released tag identifies the subassembly in which the failure occurred.

I. INTRODUCTION

The problems of detecting and locating fuel-cladding failures in an operating reactor have received much attention for a number of years. Development of instrumentation for detection of these failures has progressed much more rapidly than has the development of systems for locating them. For example, EBR-II is equipped with three devices (FERD[*], FGM[**], and RCGM[†]) that are capable of detecting when a cladding defect has occurred. These devices have been used with other diagnostic information and with a fuel-shuffling system to locate EBR-II fuel-cladding failures. However, this process is time-consuming and consequently expensive because of the prolonged shutdowns that can occur.

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[*]Failed Element Rupture Detector. Detects delayed neutrons emitted in certain fission-product decay schemes, principally from ^{87}Br.

[**]Fission Gas Monitor. Detects the radioactive alkali-metal daughters of noble-gas fission products, principally ^{88}Rb, ^{89}Rb, and ^{138}Cs.

[†]Reactor Cover Gas Monitor. Detects noble-gas fission products in the cover gas, principally ^{133}Xe and ^{135}Xe.

The difficulties encountered in locating fuel with defective cladding in EBR-II led to a search for systems which would pinpoint the location of a failure. As a result, the concept of isotopic tagging evolved. Basically, isotopic tagging involves the insertion of an isotope or a combination of isotopes into each fuel element of a subassembly in such a way that the tag will be released should the cladding fail. If a unique tag is used for each subassembly, identification of the tag will identify the subassembly in which the failure occurred.

An isotopic-tagging system, which utilizes mixtures of xenon isotopes, has been implemented in EBR-II[1] to facilitate the location of cladding defects in unencapsulated gas-bonded experimental fuels. With this type of fuel, the tag is injected into the gas bond during fabrication. Should the cladding fail, some of the gas bond containing the tag would escape and appear in the cover gas. Mass-spectrometric analysis of the cover gas can then be used to identify the ratios of specific xenon isotopes and thereby pinpoint the failure. After the defective subassembly is removed from the reactor, the tag can be removed from the cover gas by either purification or replacement of the cover gas.

This system is primarily intended for gas-bonded fuels because this type of fuel contains no materials that will impede the release of the tag once the cladding is breached. However, in EBR-II the driver fuel is sodium-bonded, and at present some of the experimental fuels are encapsulated, with a sodium bond between the fuel cladding and the capsule. In the future, sodium-bonded carbide and nitride fuels will be tested. It is believed that the bond sodium would impede or prevent the release of a gaseous tag in most defects for reasons discussed in more detail below.

Because gaseous tags were unattractive for sodium-bonded fuels, a program was initiated to develop isotopic tags for sodium-bonded driver and encapsulated fuels. This report deals with progress in this program and with the steps that must be taken to bring such tagging methods to a useful stage.

II. CRITERIA FOR THE SELECTION OF ISOTOPIC TAGS

If isotopic tagging of sodium-bonded fuel is to succeed, tags must meet the following criteria.

1) The tag must be released upon cladding failure. When a tag is introduced into a fuel element it must reside in a location which gives it the optimum probability of escaping into the primary system when the cladding fails. In the case of EBR-II driver fuel, two locations can be considered - the plenum gas and the sodium bond. EBR-II personnel[2] have made calculations to establish the equilibrium level of the sodium in a defective driver fuel while the reactor sodium pumps are running. Although these calculations were made to determine whether or not a fuel pin would become unbonded as a result of a cladding breach, the findings are also useful in establishing whether or not a gaseous tag would be released after the breach. The calculations indicate that, should a break in cladding occur in the core area, a gaseous tag would not be released in most instances. For example, at 0.95 at. % burnup, the equilibrium level of sodium after cladding failure would be above the fuel pin in all cases, and even at 1.2 at. % burnup no gas would escape unless the fuel element was in the outer rows of the core and the breach was within ∿1 in. of the top of the fuel pin. However, in most of the instances studied, bond sodium would be driven out. Thus, when sodium bonding is employed, the tag must reside in the sodium. Furthermore, since discharge of all the sodium is improbable, the tag must be homogeneously distributed, i.e., dissolved, in the bond sodium to assure release of the tag upon failure.

2) The tag must be detectable after release. This criterion imposes drastic solubility limitations on potential sodium-soluble tags. There are approximately 76,000 gal (∿3 x 10^8 g) of sodium in EBR-II's primary-coolant system. If the assumption is made that a tag concentration of 1 ppb in the bulk sodium is detectable, a back calculation reveals that at least 300 mg of tag should be added to each fuel pin. Because high concentrations of tag in the small amount (0.8 g) of bond sodium in the driver pins could appreciably change the thermal conductivity of the sodium, it seems unrealistic to use more than 100 mg of tag. Since encapsulated fuels contain ∿19 g of sodium, it seems reasonable to add at least 500 mg of tag.

A literature survey was made to obtain available data on the solubility of various elements in sodium. (It was recognized that the absence of adequate solubility data in the literature for a particular element might preclude it from further consideration; however, the scope of the program did not allow for extensive experimental work in this area.)

These solubility data were used to establish a list of potential tag elements from the standpoint of solubility.

A second restriction that affects the detectability of tags is the behavior of a tag before and after release. The tag must not be removed from the sodium by any mechanism such as adsorption on surfaces. In this regard, strontium is reported to plate out on stainless steel surfaces.[3]

Impurities already present in the sodium coolant at the ppb level may interfere with the detection of tags. Accordingly, atomic-absorption analyses[4] of EBR-II primary sodium were reviewed, and samples of EBR-II primary sodium were analyzed by radiochemical and spark-source mass-spectrometric techniques to assess the level of impurities present.

A summary of the evaluation of potential tags with respect to solubility, stability, and impurity content of EBR-II sodium is given in Table I. It can be seen that, of the elements considered, ten meet the detection requirements for encapsulated-fuel tags, whereas nine meet the requirements for driver-fuel tags.

3) Each tag must be unique and must remain unique after release.

This criterion is the essence of the isotopic-tagging concept. For isotopic tagging to be successful, a sufficient number of unique tags must be devised so that each subassembly can be tagged with a distinguishable tag. EBR-II, for example, would require between 75 and 100 separate tags. To manufacture this many tags within the restrictions discussed above requires that mixtures of isotopes in varying ratios must be used. The fact that the isotopic ratio of the tag must remain unique, both before and after release, suggests but does not require that the tags be made up of isotopes of the same element (i.e., isotopes of the same element would exhibit similar behavior, and any minor losses would not affect the ratio).

4) A tag, once released, must not interfere with identification of tags released in subsequent failures. The identification of a tag released when the first cladding failure occurs will present no problem. However, subsequent releases will become progressively more difficult to identify if previous tags are still detectable. For example, in sodium containing a previously released tag with an isotopic ratio of 25/75, a new isotopic ratio of 50/50 can be produced by the release of any tag having an isotopic ratio greater than 50/50. Admittedly, concentration measurements before and after release in conjunction with an isotopic analysis could be used

TABLE I. Summary of Solubility Data and Other Factors
Affecting Detection of Tags

Element	Solubility[a] in Sodium at 900°F (at. %)	Solubility (at. %) Required for Encap- sulated-Fuel Tag	Solubility[b] (at. %) Required for Driver- Fuel Tag
Ag[c,d]	6.3	0.57	2.7
Au	35	0.31	1.5
Ba	40	0.45	2.1
Bi[c]	1	0.3	
Cu[c]	2	1.53	
Cd	M	0.55	2.6
Cs[d]	M	0.46	2.2
Ga	3	0.88	
Hg	M	0.31	1.5
K[e]	M	1.56	7.3
Pb[c]	M	0.30	1.4
Rb[e]	M	0.72	3.4
Sb	7.3	0.51	2.4
Se	13.3	0.78	3.6
Sn[c,d]	40	0.52	2.4
Sr[f]	8	0.70	3.3
Te	5	0.48	2.3
Th	5	0.27	1.3
Tl	M	0.30	1.4

[a]M = Complete miscibility.

[b]Blank spaces indicate a concentration requirement greater than the solu-
bility at 900°F.

[c]Naturally occurring elements detected in EBR-II sodium by spark-source
mass spectrometry or atomic-absorption spectrometry.

[d]Naturally occurring elements detected in EBR-II sodium by radiochemical
techniques.

[e]Elements expected in sodium as natural contaminants.

[f]Reported to plate out from sodium onto stainless steel.

to identify the second defective fuel element (and possibly the third and fourth), but eventually the situation would become so complex that it would be unresolvable. Thus, tagging systems using analytical techniques which measure the isotopic ratio and concentration of stable isotopes are unattrac- unless the released tags are removed.

5) <u>The tag must not be detrimental to the reactor</u>. This criterion requires that neither the concentrated tag in the fuel element nor the released, diluted tag will create corrosion, pressure, thermal-conductivity, or nuclear problems.

III. SELECTION OF DETECTION METHOD

A survey of possible detection methods showed that three methods would be capable of providing the necessary sensitivity for identifying a tag in the primary sodium coolant; these are spark-source mass spectrometry, out- of-reactor thermal neutron activation, and gamma-spectrometric assay for tag activation products produced while the tag is in the core of the reac- tor. The first two methods were rejected because, as previously discussed, the identification of released tags is complicated unless the tags from previous releases have been removed. Within the present operational re- straints of EBR-II, no purification other than cold trapping is available, and cold trapping would not remove previously released tags effectively enough to eliminate interference. The third method of detection, gamma- spectrometric assay for tag activation products, does not require removal of the tags providing the selected tags have activation products with suitably short half-lives. This freedom from interference from previous tags is explained in more detail below.

IV. TAGGING METHODS

Two tagging methods have been devised that show promise for use in tagging sodium-bonded fuels. The first involves the use of mixtures of gold and antimony; the second, mixtures of gold and platinum.

A. <u>Gold-Antimony Tagging Method</u>

In the proposed gold-antimony method, each fuel element in a subassembly would be tagged with the same mixture of ^{197}Au and ^{121}Sb; the weight ratios of ^{197}Au and ^{121}Sb would be varied to produce multiple tags. While in the core of EBR-II, these tag mixtures would be activated to pro- duce ^{198}Au (2.7 d) and ^{122}Sb (2.8 d). Because of the varying weight ratios,

each activated tag mixture would have a distinctive activity ratio. In the event of a cladding defect, the active isotopes would be discharged to the primary coolant. After appropriate sampling and separation procedures, the ^{198}Au/^{122}Sb activity ratio would be determined by gamma-ray spectrometry, and this ratio would be used to identify the subassembly containing the faulty fuel element. The details of this method are discussed below in relation to criteria previously discussed.

Calculations were made of the level of activity of ^{198}Au that would be produced from irradiation of ^{197}Au in the core of EBR-II at full power; the value used for the capture cross section of ^{197}Au in EBR-II was 200 mb.[5] These calculations showed that (1) the saturation activity of ^{198}Au produced from 1 mg of ^{197}Au would be about 6×10^8 dps ($\sim$98% of saturation is achieved in 15 days) and (2) the activity produced in one day would be about 1.2×10^8 dps/mg of ^{197}Au. Release of 1 mg of ^{197}Au of the latter level of activity to the 3×10^8 g of sodium coolant would result in a ^{197}Au activity level in the sodium of 0.4 dps/g of sodium. This level of activity should be more than adequate for detection in a 10-g sodium sample after appropriate radiochemical separations have been performed.

Because experimental data on the capture cross section of ^{121}Sb were not available, differential cross sections were estimated with the NEARREX computer code,[6] and these were summed over a typical EBR-II flux spectrum. The results of the calculation indicated a capture cross section for ^{121}Sb in EBR-II of about 70 mb, which should produce sufficient ^{122}Sb to be detectable.

A distinct advantage accrues from using the ^{121}Sb and ^{197}Au isotopes as tags because of the similarity in the half-lives of the daughter activities (^{122}Sb, 2.8 d; ^{198}Au, 2.7 d). During irradiation in the core of EBR-II, the ratio of ^{198}Au to ^{122}Sb activities produced will be nearly constant. For example, if one assumes that the saturation activity ratio will be 1.00, the activity ratio after one hour of irradiation will be 0.961, and, thereafter, will approach 1.00. The constancy of the activity ratio would permit numerous tags to be manufactured from these two isotopes. The exact number of tags that could be put into use would depend on the constancy of the ratio of the capture cross sections of ^{197}Au and ^{121}Sb as a function of neutron energy and on the precision of the radiochemical separations used to isolate the active isotopes. It is estimated that as many as 100 tags could be made.

Until suitable methods of purifying the primary coolant are devised, any tagging method must consider the effects of previously released tags. Although most potential methods would require purification of the coolant to remove previous tags, the gold-antimony method is reasonably free from the effects of previous tags, as can be seen from the discussion below.

Prior to release, a fuel-element tag would reside in the core of the reactor 100% of the time, and as previously stated, would achieve a saturation activity level of about 6×10^8 dps/mg of ^{197}Au. Any ^{197}Au already in the circulating sodium would spend only about 1/2000 of the time in the core, and the saturation level would be expected to be about 3×10^5 dps/mg of ^{197}Au. A simple calculation shows that the circulating sodium must contain approximately 2 g of ^{197}Au before the activity level will be equal to that produced in the core in 1 mg of ^{197}Au tag. Furthermore, a tag that has achieved the saturation activity level of 6×10^8 dps/mg of ^{197}Au in the core will decay rapidly to the lower saturation level of 3×10^5 dps/mg of ^{197}Au once it is released to the sodium.

In selecting a tag, consideration must also be given to the corrosiveness of the tag toward the fuel cladding. In preliminary studies to test the corrosion characteristics of possible tags in a fuel-element environment, gold and antimony were among the elements tested. Mixtures of Na-2 wt % Sb and Na-2 wt % Au were placed in separate capsules of Type 304L stainless steel, which were then sealed and rotated at 650°C for 500 hr. Metallographic examination revealed that the stainless steel was not attacked by either gold or antimony under these conditions.

One potential difficulty in the gold-antimony system may be with the stability of the tag both before and after it is released. Alteration of the gold-to-antimony ratio by any mechanism (e.g., selective adsorption on stainless steel) would severely limit the tag's usefulness.

B. Gold-Platinum Tagging Method

The second tagging method, which utilizes mixtures of isotopes ^{197}Au and ^{198}Pt, would operate on the same general principles as the gold-antimony method. In this case, however, tag identification would be made on the basis of the ^{198}Au/^{199}Au activity ratio. The ^{199}Au is produced by the reactions

$$^{198}\text{Pt}(n,\gamma)^{199}\text{Pt} \xrightarrow[\text{(31 m)}]{\beta^-} {}^{199}\text{Au}(3.15 \text{ d})$$
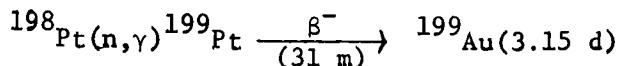
Estimations of the capture cross section of ^{198}Pt in EBR-II, made by the method described above, indicate a value of the same magnitude as that of ^{121}Sb, namely, about 70 mb. Therefore, as in the case of ^{122}Sb, the activity level of ^{199}Au in the sodium coolant should be adequate for detection.

One attractive feature of the gold-platinum tagging method is that tag identification is made on the basis of the ratio of two isotopes of the same element in the sodium coolant. Therefore, a minor instability of gold in the reactor system would produce no alteration in the ^{198}Au/^{199}Au ratio of a released tag.

Only fragmentary information is available in the literature on the solubility of platinum in sodium (for this reason, platinum was not listed in Table I), and the possibility exists that the solubility may not be high enough for platinum to be used as a tag for driver fuel.

Another disadvantage in the gold-platinum method is that during variations in reactor operating conditions, the ^{198}Au/^{199}Au activity ratio would not be as constant as the ^{198}Au/^{122}Sb activity ratio. The reasons for the greater variation in the ^{198}Au/^{199}Au activity ratio are as follows: (1) The half-life of ^{122}Sb (2.8 d) is more nearly equal to the half-life of ^{198}Au (2.7 d) than is the half-life of ^{199}Au (3.15 d). (2) The formation of ^{199}Au is delayed by the 31-min half-life of the intermediate activation product ^{199}Pt.

C. Comparison of the Two Methods

To gain some insight into how much variation would be produced by reactor startups, shutdowns, and changes in power, calculations were made which permitted comparison of the performance of a ^{197}Au-^{198}Pt tag with that of a ^{197}Au-^{121}Sb tag during a one-month period of operation of EBR-II. The following assumptions were made in performing the calculations:

(1) Each tag is composed of equal weights of ^{197}Au and the other isotope.

(2) The capture cross sections are 200 mb for ^{197}Au, and 70 mb for both ^{198}Pt and ^{121}Sb.

(3) The time to achieve the power level and the time to shutdown are insignificant.

The results of these calculations are given in Table II. It is evident from these results that identification of a gold-platinum tag

TABLE II. Calculated Activity Ratios of Tags During a
Typical EBR-II Operating Period[a]

Time Interval (days)	Power (MW)	Activity Ratio at End of Interval	
		$^{198}Au/^{122}Sb$	$^{198}Au/^{199}Au$
3.5	30	1.79	3.19
7.0	0	1.68	2.43
2.5	30	1.78	3.10
1.0	0	1.77	2.95
3.25	30	1.78	3.04
1.25	0	1.76	2.87
3.25	30	1.77	2.98
3.25	0	1.72	2.62
2.5	30	1.76	2.95
3.5	50	1.78	3.02

[a]Period from Oct. 1 to Oct. 31, 1968.

would be more difficult than identification of a gold-antimony tag because the variations in activity ratios are greater. However, with adequate failure-detection equipment and a power record of the reactor, tag identification could be made.

V. CONCLUSIONS AND RECOMMENDATIONS

Both of these methods were considered to be feasible tagging methods at the time that the level of funding required the termination of the program. However, a number of additional experiments will be necessary before a final decision can be made about the practicality of implementing either method. These experiments and their objectives are discussed in the paragraphs below.

Additional information on the solubility of platinum in sodium must be obtained.

The stability of sub-ppb quantities of gold and antimony in the EBR-II environment must be tested. The possibility of performing such stability tests in the EBR-II primary coolant should be investigated. The most definitive experiments would be to activate milligram quantities of ^{197}Au, ^{121}Sb, and ^{198}Pt to saturation before charging them in known activity ratios to the EBR-II primary system. By following the activity ratios, the stability of the tags in the system could be established or negated. The final level of activity would also substantiate the activity levels to be expected from tags that are present in the circulating sodium.

The stability of relatively concentrated (100 mg tag/0.8 g Na) solutions of gold-antimony and gold-platinum in sodium must be tested. In this regard it may be necessary to investigate (1) the sodium-rich corner of the ternary phase diagrams of Au-Na-Sb and Au-Na-Pt, (2) the behavior of tags in contact with stainless steel, and (3) the behavior of tags in contact with stainless steel and metal, carbide, and nitride fuels.

Corrosion behavior of gold-antimony and gold-platinum in sodium toward stainless steel must be established in long-term tests. Some information has been obtained from separate experiments involving gold and antimony but no corrosion information is available about either tag pair.

Data on the fast capture cross sections of the tag materials must be obtained in the neutron energy range of EBR-II. These need not be absolute data; relative data between ^{197}Au and ^{121}Sb and between ^{197}Au and ^{198}Pt as

a function of energy will be adequate. This type of data could most readily be obtained by differential cross-section measurements.

Methods of isolating and detecting tags must be investigated. Distillation of the bulk of the sodium would concentrate the tag and reduce the ^{24}Na activity to a reasonable level. In this regard, distillation equipment capable of handling 100-g samples of sodium has been tested on the secondary sodium system of EBR-II and should be installed on the primary sodium system by the end of calendar year 1971. In the determination of trace impurities in EBR-II sodium, gamma spectrometry has been demonstrated to be applicable to the analysis of primary sodium, after suitable radiochemical separations have been made. Experiments must be performed, however, to demonstrate the overall procedure involving distillation, radiochemical separations, and gamma-spectrometric analysis.

Experiments must be performed to ascertain the number of tags that can be manufactured from gold-antimony and gold-platinum. Such considerations as changes in the capture cross-section ratios as a function of neutron energy and the overall analytical precision should be factored into these experiments. In setting the ratios for the tags, the possibility of devising a simple computer program to increase the reliability of tag identification should be considered.

Methods of introducing tags into fuel elements must be investigated. Initially, weighed quantities of gold and antimony or platinum might be introduced separately. Eventually, however, an optimum method that can be implemented on a "production-line" basis must be developed.
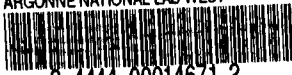
ACKNOWLEDGMENTS

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